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Liquid-liquid equilibria of water + ethanol + 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ternary system: measurements and correlation at different temperatures

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ABSTRACT

In this work, the experimental liquid-liquid equilibria (LLE) data of water + ethanol + 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][Tf2N]) system at different temperatures is presented. The LLE of the systems has been measured between 283 and 323 K. The NRTL and UNIQUAC models were applied to the ternary systems. The interaction parameters obtained from both models successfully correlated the equilibrium compositions, however UNIQUAC gave a more accurate correlation. Finally, the solvent capability of ionic liquid was checked in order to separate the mixture formed by ethanol and water.

KEYWORDS

Liquid–liquid equilibria; ionic liquid; 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide ([bmim][Tf2N]); ethanol; water.

1. INTRODUCTION

Ethanol is used currently as a common solvent and as an additive to gasoline. Moreover, bioethanol is one of possible renewable energy sources that can be produced from several feedstock using biotechnology processes. One of the major hurdles in switching to a biomass-based industry is the production costs (both, economic and energetic) of the base alcohols. Purifying an alcohol requires about 6% of the energetic value of the compound itself, with a large portion used in the separation of the alcohol from the fermentation broth, mainly composed of water[1]. So, during the last years many different processes have been examined for the recovery of near anhydrous ethanol[2]. Conventionally, separating ethanol and water requires a series of distillation columns and it is limited due to the presence of the azeotropic point of the binary system. So this method is energetically costly, and much room for improvement exists. Recent development of new membrane technology, such as pervaporation, has improved the efficiency of this separation, although rapid fouling of the membranes remains a major issue with these methods[3]. For this reason, the elimination of the azeotrope was investigated with the use of ionic liquids (ILs) as entrainers for the extractive distillation[4-6].

ILs are salts with a melting point below 100 ºC, which are usually composed of a poorly coordinating, bulky organic cation, and an organic or inorganic anion. Some of the properties that make them advantageous for this application are the negligible vapour pressure, which allows for recovery and reuse of the ionic liquid (IL); a large liquid range, which allows for ease of separation; and, finally, a versatility which allows the creation of ILs that preferentially select

alcohols from water[7-8]. ILs as extraction solvents possess certain advantages which allow them to replace conventional toxic or flammable organic solvents. Their most important properties are: (a) they exhibit a wide liquid range, (b) good thermal stability, (c) solvation of a wide spectrum of substances, (d) not traceable vapour pressure and (e) and extraordinary degree of versatility[9].

For these reasons it has been shown that ILs have the potential for separating alcohol/water mixtures with simple liquid-liquid extraction[10], which could be less energetically costly than distillation, and would have limited fouling problems.

A few groups have studied ternary systems of ILs, alcohols and water. Some of them have study the separation of binary mixture 1-butanol and water using ILs[11-14]. This work is focused on the binary mixture ethanol + water. There is a variety of ternary vapour-liquid equilibrium (VLE) data available for ILs with ethanol and water[15-20] but there is scarce data about the liquid-liquid equilibrim (LLE) of the ternary system IL+ethanol+water[21-22]. Swatloski et al.[21] studied the possibility of use as solvents in liquid-liquid extraction some hydrophobic hexafluorophosphate ionic liquids and Chapeaux et al. the 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[22].

This study focusses on accurately measuring the fundamental data necessary to design and implement liquid-liquid extraction for the separation of ethanol from water, presenting the experimental tie lines at different temperatures for the ternary mixtures 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf2N]), ethanol and water. In a recent literature review not LLE data for this system has been found. In addition, we focus on the modelling of the phase behaviour, which is important in the design of real extraction processes.

The LLE data were correlated using the UNIQUAC[23] and NRTL[24] activity coefficient models. Finally, the solvent capability of ionic liquid was tested through the distribution coefficient determination.

2. EXPERIMENTAL SECTION

2.1. Chemicals

[Bmim][Tf2N] (w > 0.99) was provided by iolitec. Ethanol (w = 0.99, assay GC) was supplied from Fluka and water was bidistilled. The reagents were used without further purification after chromatography failed to show any significant impurities. A chemical sample description is given in Table 1. Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (w < 0.0005). Appropriate precautions were taken when handling the reagents in order to avoid hydration. The densities of the pure components were measured at 298.15 K using an Anton Paar DMA 58 densimeter, and the refractive indexes were measured at 298.15 K using an Abbe refractometer Atago 3T. Temperature was controlled to ± 0.01 K with a thermostated bath integrated on the equipment. The uncertainty in density and refractive index measurements are ± 0.01 kg·m-3and ± 0.0002, respectively. The experimental values of these properties are given in Table 2.

2.2. Apparatus and procedure

The equipment used and the procedure for the determination of liquid-liquid data has been described in a previous work[29]. Equilibrium data were obtained by preparing mixtures with a

bulk composition in the two-phase region which were placed in test tubes which were filled almost completely. The mixtures were intensively stirred for ten hours (50 times by minute) and allowed to settle for at least 12 h at constant temperature. The time necessary to attain equilibrium was established in preliminary experiments. The temperature was controlled with a thermostated bath (UNITRONIC ORBITAL from SELECTA with an incorporated stirring system). The uncertainly of the temperature measurements was ± 0.1 K (measured with an Amarell thermometer, with calibration certificate, supplied by VWR). Then, samples were taken from both phases and analyzed by gas chromatography and the gravimetric method.

2.3. Analysis

The composition of the sampled liquid phases was determined using an equipment developed by our research group (utility model application number U201400643, filed at the SPTO, on 25/07/2014) following the steps described below.The first step is the separation of volatile compounds by microdistillation.

The relative composition of volatile compounds is determined using a Series chromatograph equipped with a thermal conductivity detector (TCD), an HP3395 integrator and a 2 m x 1/8 in column packed with Porapack Q-S 80/100. Column, injector and detector temperatures were 443, 453 and 473 K, respectively. Very good peak separation was achieved under these conditions and calibration analyses were carried out to convert the peak area ratio to the mass composition of the samples. In order to obtain homogeneous mixtures of the standard, methanol has been added to the calibration and sample vials. In general, at least two analyses were made of each liquid composition. The uncertainty in the mole fraction was usually less than 0.001.

Finally the total amount of volatile compounds and ionic liquid on the sample was gravimetrically established after eliminating the volatile components from a known mass of

sample by evaporation to dryness. For this process was used a block heater from Stuart (model SBH130DC), starting with a temperature of 353 K and rising to 443 K, until constant weight. With the method of analysis developed all the compositions of the components of system were determined experimentally.

3. RESULTS AND DISCUSSION

3.1. Experimental data

The determination of composition of the equilibrium liquid phases for water (1) + ethanol (2) + [bmim][Tf_2N] (3) system were carried out at 283.2, 303.2 and 323.2 K at atmospheric pressure. The experimental data for the system are presented in Table 3 and Figures 1 to 3. All concentrations are expressed in mole fractions.

As can be observed in Figures 1 to 3 the liquid-liquid phase diagrams for the system are type I, where only one binary subsystem has partially miscibility and two binary subsystems are miscible [30]. So, the [bmim][Tf_2N] and water binary system shows a large immiscibility gap, and the binaries ethanol + water, and [bmim][Tf_2N] + ethanol are completely miscible. The ternary systems exhibits a large two-phase region meaning from the IL/water binary. The size of immiscibility gap is adequate for extraction but the slope of tie lines is suitable for the water (1) + ethanol (2) + [bmim][NTf2] (3) at all temperatures studied, indicating that ethanol has a higher affinity toward the IL than toward the water.

The addition of IL to the ethanol/water mixture increases the solubility of ethanol in the IL rich phase, while only slightly increasing the solubility of the ionic liquid in the water rich phase, which in all cases is low (<0.02). So, the presence of IL in raffinate stream will be really low. This is an important advantage of ILs used as a solvents, since this fact could reduce the number

of purification steps in the extraction unit, reducing operating costs. This behavior is observed in all the isotherms obtained in this work.

For water (1) + ethanol (2) + [bmim][Tf_2N] (3) system there is a significant temperature influence, as was shown in Figure 4. Anyway, the immiscibility zone is increasing with decreasing temperature. On the other hand, the slope of tie lines is more adequate with increasing the temperature. So, there are two opposite effects, which is discussed afterwards taking into account the distribution ratio.

The reliability of experimental results (tie-lines) can be ascertained by applying the Othmer-Tobias correlation[28]:

$$\left[(1-w_1)/w_1\right]_{organic\ phase} = a\ \left[(1-w_3)/w_3\right]^{b}_{aqueous\ phase} \qquad (1)$$

where w_1 is the mass fraction of water; w_3 is the mass fraction of ionic liquid and *a* and *b* are constants in Eq. (1). Figure 5 shows the plot on logarithmic scale of $\left[(1-w_1)/w_1\right]_{aqueous\ phase}$ against $\left[(1-w_3)/w_3\right]_{IL\ phase}$ at all temperatures for the system under study. The linearity of these plots indicates the degree of consistency of related data. The parameters of this correlation are given in Table 4.

3.2. Data correlation

The experimental LLE data for the ternary systems at three different temperatures have been correlated. To calculate liquid phase activity coefficients the excess Gibbs energy models UNIQUAC[23] and NRTL[24] have been used. The Chemcad regression tool has been used to fit

parameters to measured data. Since the simulation software database does not provide any data of the [bmim][Tf_2N], pure component properties need to be introduced. The minimum required data for the liquid-liquid correlations are the molecular weight, the UNIQUAC area (q) and volume (r) parameters[25] and the vapor pressure. Taking into account that the ionic liquids have negligible vapor pressure, proper fictional constants of the Antoine's equation have been fixed for the [bmim][Tf_2N]. Temperature dependency of the binary interaction parameters has not been considered. To fit the UNIQUAC interaction parameters, the structural parameters (r and q) recommended by DECHEMA[26] and Seoane et al.[28] were used for the pure components and are listed in Table 2. The non-randomness parameter (α_{ij}) of the NRTL equation given on Table 5 have been fixed to 0.2 or 0.3, as the value recommended by literature for such systems[24, 28], and maintained in all cases. Finally, the α parameter of the NRTL model has been keep constant at 0.3, since some correlations have been done with α parameter equal to 0.2 without further improvement of the deviations.

There are two effective binary interaction parameters for a binary subsystem. Therefore, six effective binary interaction parameters are required for a ternary system. The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and calculated equilibrium mole fractions for each of the components for all the experimental tie lines. The objective function (OF) used is:

$$OF = \sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{3} (x_{ijk} - \hat{x}_{ijk})^2 \qquad (2)$$

$\hat{x}$ the calculated mole fraction, and subscripts i, j and k denote, respectively, component, phase and tie line.

The correlation of experimental data was carried out separately at each temperature. The binary interaction parameters calculated in this way are given in Table 5. Also the root-mean-square deviation (rmsd) of the phase composition is included in this table:

$$rmsd = 100 \cdot \left(\sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{3} \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right)^{1/2} \qquad (3)$$

The rmsd is a measure of the agreement between the experimental and calculated data.

The parameters obtained are tested for each of the temperatures using the commercial program HYSYS from Aspentech.

In Table 5 it can be observed a good agreement between UNIQUAC correlations and experimental data, supporting the reliability of the parameters obtained. However, the NRTL model has obtained a slightly worse correlation.

In Figures 1 to 3, the experimental data at 283.2, 303.2 and 323.2 K have been plotted for water (1) + ethanol (2) + [bmim][Tf_2N] (3) together with binodal curves calculated using the UNIQUAC and NRTL models, experimental tie lines and calculated tie lines using UNIQUAC model.

Although a relatively good fit is obtained for each temperature, the parameters determined have no relation between them.

3.3 Study of capability of [bmim][Tf2N] *as solvent*

A study of capability of ionic liquid as a solvent in the separation of the azeotropic mixtures water (1) + ethanol (2) by liquid-liquid extraction was made. The immiscibility zone and their shape is adequate, so the [bmim][Tf_2N] can be considered as a relatively good solvent. The distribution coefficient was defined as:

□□ = □□,[bmim][Tf2N] □□□ℏ □ℏ □□□□□, □□□□□ □□□ℏ □ℏ □□□

(3)

where *s* is the solute ethanol (2), and provided in Table 3. In Figure 5 the effect of the solvent in the distribution of ethanol (2) in both liquid phases is visualized. In this figure we not include the distribution coefficients of systems ethanol/water with other ionic liquids because they are type II systems or the information provided by author not allow calculate this parameter[4,11,12,21,22]. As can be observed, the separation seems effective, increasing the distribution coefficient with increasing temperature, although the immiscibility zone is smaller.

For water (1) + ethanol (2) + [bmim][NTf2] (3), in all cases the distribution coefficient is greater than the unity, so the extraction became feasible. Furthermore, his value is three time greater with increasing the extraction temperature to 323.2 K.

For low concentrations of ethanol in water, the distribution coefficient has the best values, although due to the molecular weight of the ionic liquid and water are so different and the slope of tie line, the extraction process requires a large amount of solvent. Also because the distribution coefficient is comparatively close to unity in some cases. But that should not be considered a drawback due to the easiness of their recuperation.

The effectiveness of a solvent can be expressed by the selectivity S. In fact, the effectiveness of methanol extraction by water is given by its selectivity, which is an indication of the ability of water to separate methanol from DMC, and is given by:

$$S = \frac{(x_2 / x_1)_{aqueous\ phase}}{(x_2 / x_1)_{organic\ phase}} \quad (4)$$

Where the subscript 1 represents DMC and 2 represents methanol. As shown in Table 2, the selectivity values are greater than 1 (these values vary between 3 and 77) for the system reported here, which means that extraction of methanol by water is possible. The selectivity values are not constant over whole two phase region; they decreased as the concentration of methanol increased; therefore the higher the concentration of methanol in the feed the lower the selectivity of water. The extracting power of the solvent (water) at each temperature is shown in Figure 3 and it can be observed that the higher the temperature, the lower the selectivity.

Finally, it can be concluded that the [bmim][Tf2N] can be consider as a solvent for the separation of water (1) + ethanol (2) mixture.

4. Conclusions

Developing an understanding of the behaviour of ternary systems with ionic liquids is a critical first step in determining their ability to separate systems such as alcohols and water. Furthermore, one must have experimental data in order to obtain reliable parameters of models, which allow their use to simulate the process with guaranties.

The determination of composition of the equilibrium liquid phases for the system water (1) + ethanol (2) + [bmim][Tf_2N] (3) was carried out between 283.2 and 323.2 K.

The UNIQUAC [23] and NRTL [24] models were used to correlate the experimental data. Both models were found to properly correlate the data for the two systems studied. However, a slightly worse correlation has been obtained by the NRTL model.

In order to study the viability of liquid-liquid extraction, the capability of ionic liquid as solvent was assessed through the distribution coefficient. This parameter increase with increasing the temperature, so this operation variable must be considered in the extraction design.

It can be concluded that the [bmim][Tf_2N] can be considered as a relatively good solvent for the separation of the mixture water (1) + ethanol (2) .

List of symbols

A	*interaction parameters*
M	*number of tie lines*
n_D	*refractive index*
OF	*objective function*
q	*area parameter in UNIQUAC equation*
r	*volume parameter in UNIQUAC equation*
rmsd	*root mean square deviation*
x	*composition of liquid phase, mole fraction*
K	*distribution coefficient*

Greek letter

α	*non-randomness factor in NRTL equation*
ρ	*density*

Superscripts

^	*calculated*

Subscript

i	*component i*
j	*component j*
k	*component k*
m	*group m*
n	*group n*
s	*solute*

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FIGURES

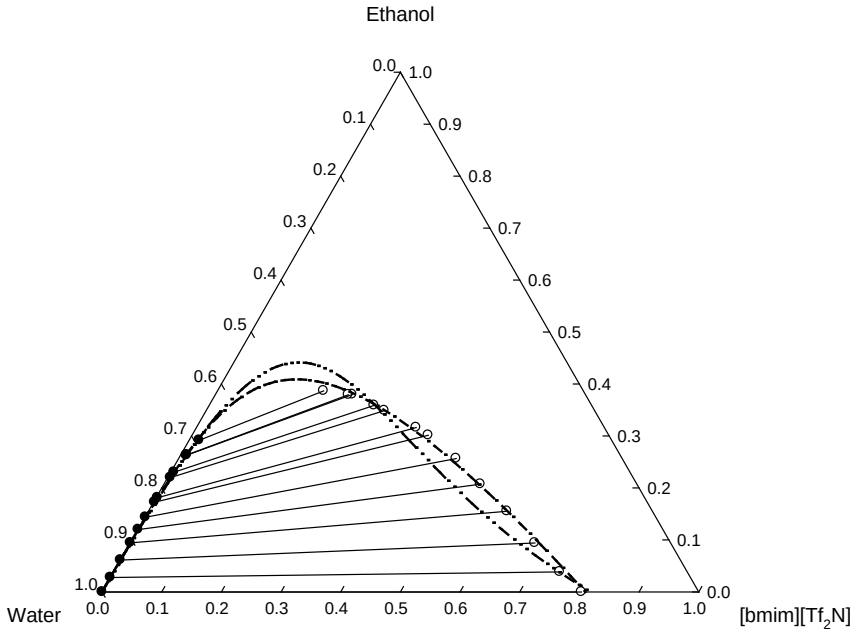

Figure 1. Liquid-liquid equilibria of the water (1) + ethanol (2) + [bmim][Tf_2N] (3) system at *T* = 283.2 K. Experimental data (○) [bmim][Tf_2N] rich–phase, (●) aqueous phase, (—) experimental tie lines. Binodal curve calculated using: (- - -) UNIQUAC model, (··—··—··) NRTL model

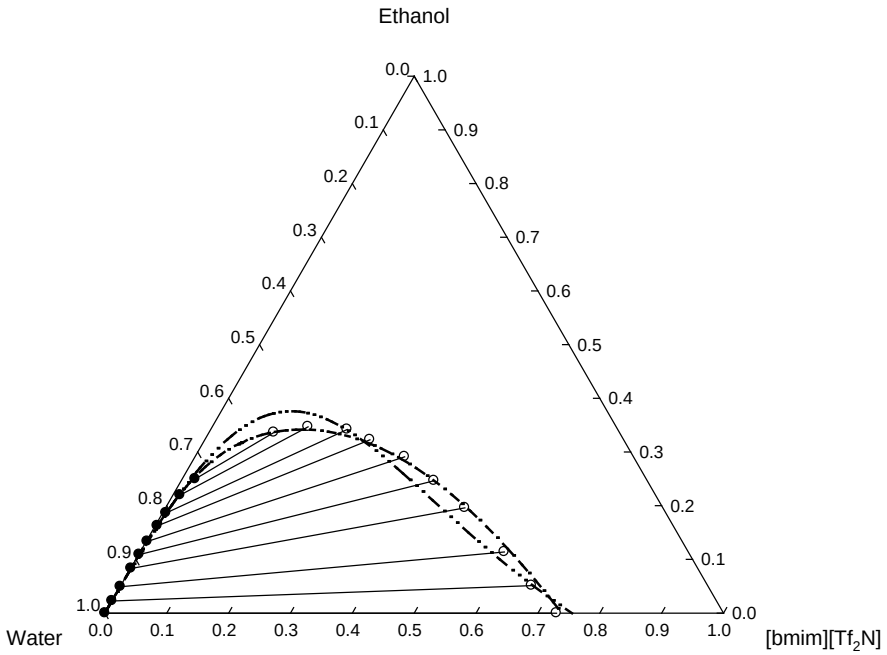

Figure 2. Liquid-liquid equilibria of the water (1) + ethanol (2) + [bmim][Tf_2N] (3) system at *T* = 303.2 K. Experimental data (○) [bmim][Tf_2N] rich–phase, (●) aqueous phase, (—) experimental tie lines. Binodal curve calculated using: (- - -) UNIQUAC model, (··—··—··) NRTL model.

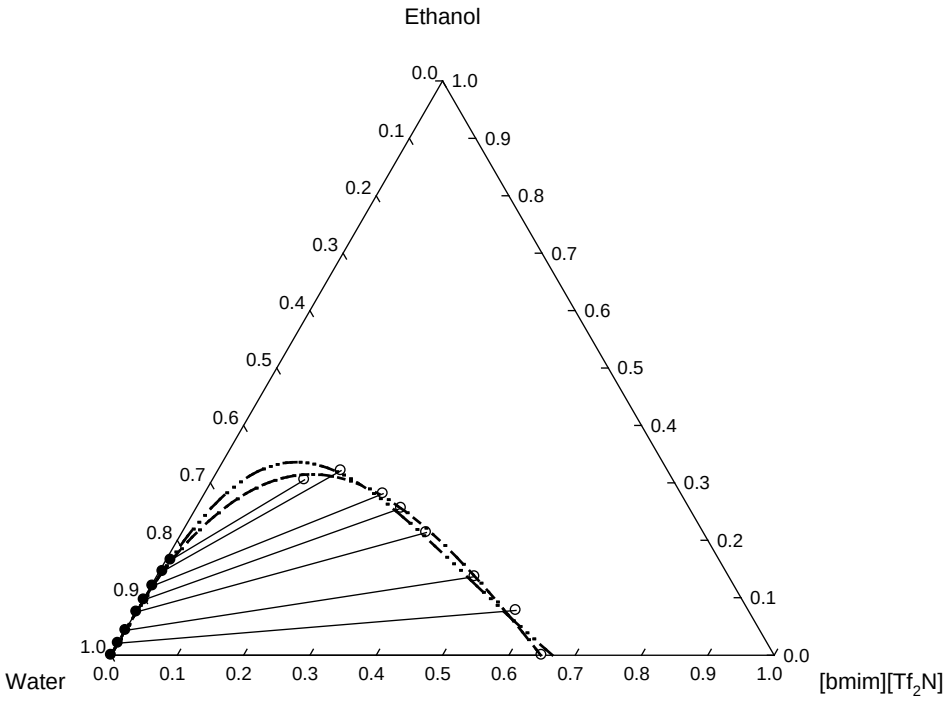

Figure 3. Liquid-liquid equilibria of the water (1) + ethanol (2) + [bmim][Tf_2N] (3) system at *T* = 323.2 K. Experimental data (○) [bmim][Tf_2N] rich–phase, (●) aqueous phase, (—) experimental tie lines. Binodal curve calculated using: (- - -) UNIQUAC model, (··—··—··) NRTL model.

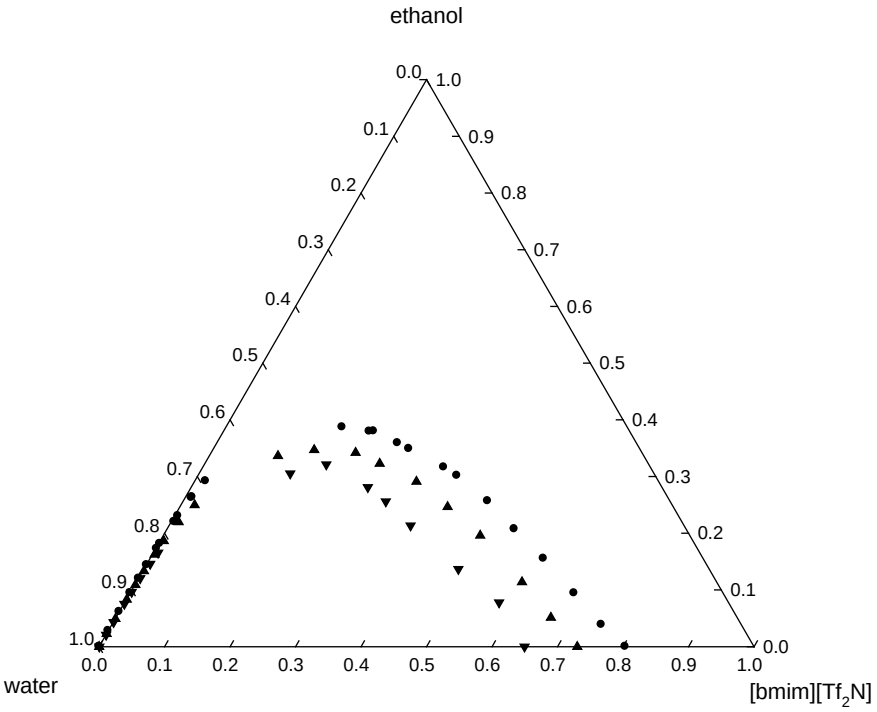

Figure 4. Influence of temperature on liquid-liquid equilibrium of the water (1) + ethanol (2) + [bmim][Tf_2N] (3). (●), experimental data at 283.2 K; (▲), experimental data at 303.2 K; (▼), experimental data at 323.2 K.

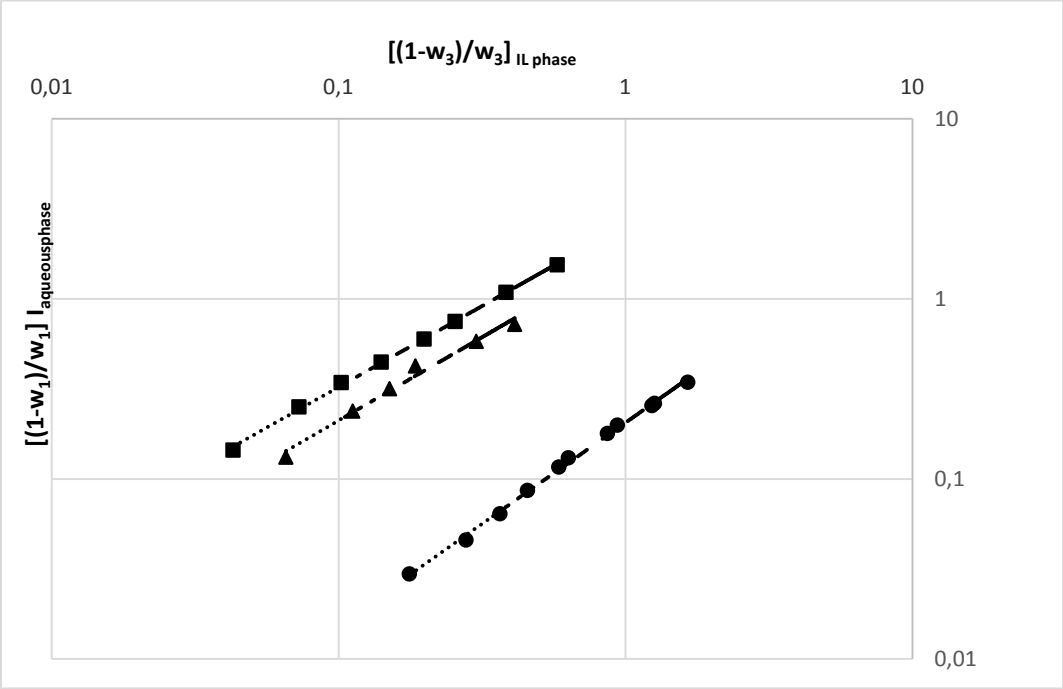

Figure 5. Othmer-Tobias plot of the water (1) + ethanol (2) + [bmim][Tf_2N] (3) system. Experimental data: (●) 283.15 K, (▲) 303.2 K, (■) 323.2 K. Calculated curve: (…).

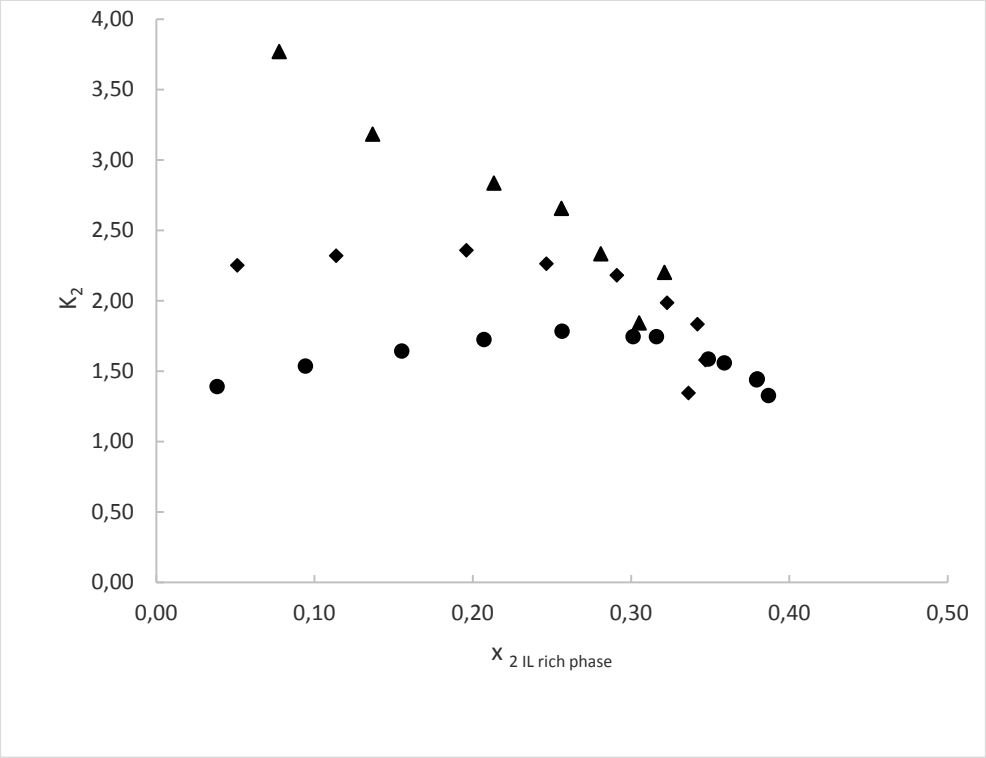

Figure 6. Distribution coefficient of ethanol between the extract and raffinate phases for the water (1) + ethanol (2) + [bmim][Tf_2N] (3) system: (●) 283.2 K, (♦) 303.2 K, (▲) 323.2 K.

TABLES.

Table 1. Chemical sample description.

Chemical Name	*Source*	*Purity (mass fraction)*	*Purification Method*	*Analysis Method*
water	Fluka	0.9950	none	GC
ethanol	Fluka	0.9980	none	GC
[bmim][Tf_2N]	Iolitec	> 0.9900	none	Gravimetric
methanol	Across Organics	0.9997	none	GC

Table 2. Density ρ, Refractive Indexes n_D and UNIQUAC Structural Parameters of Pure Components.

Component	*ρ (kg m^{-3}) (298.15 K)*		*n_D (298.15 K)*		*UNIQUAC parameters*	
	Exptl.	Lit.[a]	Exptl.	Lit [a].	r[b]	q[b]
water	997.06	997.05 [a]	1.3325	1.3325 [a]	0.9200[b]	1.3997[b]
ethanol	786.47	785.01 [a]	1.3594	1.3594 [a]	2.5755[b]	2.5880[b]
[bmim][Tf_2N]	1434.23	1436.00 [c]	1.4267	1.4265 [c]	11.20 [d]	10.20[d]

[a]Taken from TRC tables[25].

[b]DECHEMA[26].

[c] Tariq et al.[27].

[d] Seoane et al.[28].

Table 3. Experimental liquid-liquid equilibrium data at 101.30 kPa of the system water (1) + ethanol (2) + [bmim][Tf_2N] (3)[a].

T (K)	*[bmim][Tf_2N] rich phase*		*Water rich phase*		K_2	S_2
	x_1	x_2	x_1	x_2		
283.2	0.1964	0.0000	0.9997	0.0000	-	-
	0.2135	0.0386	0.9720	0.0277	1.391	6.331
	0.2273	0.0943	0.9382	0.0614	1.536	6.341
	0.2436	0.1552	0.9051	0.0945	1.643	6.105
	0.2622	0.2073	0.8792	0.1202	1.725	5.785
	0.2781	0.2566	0.8553	0.1437	1.785	5.490
	0.3025	0.3015	0.8255	0.1727	1.746	4.765
	0.3523	0.3490	0.7754	0.2199	1.587	3.492
	0.3644	0.3590	0.7642	0.2303	1.559	3.269
	0.3907	0.3799	0.7274	0.2628	1.446	2.691
	0.3155	0.3162	0.8165	0.1812	1.745	4.516
	0.3973	0.3794	0.7257	0.2638	1.438	2.627
	0.4351	0.3870	0.6912	0.2917	1.326	2.107
303.2	0.2698	0.0000	0.9997	0.0000	-	-
	0.2844	0.0512	0.9769	0.0227	2.252	7.735
	0.2972	0.1138	0.9504	0.0491	2.320	7.419
	0.3201	0.1961	0.9161	0.0832	2.358	6.749
	0.3445	0.2466	0.8899	0.1089	2.264	5.848
	0.3697	0.2912	0.8647	0.1334	2.182	5.103
	0.4102	0.3228	0.8339	0.1626	1.985	4.036
	0.4372	0.3421	0.8079	0.1865	1.834	3.390
	0.4978	0.3471	0.7686	0.2197	1.580	2.439
	0.5586	0.3363	0.7291	0.2499	1.346	1.757
323.2	0.3503	0.0000	0.9996	0.0000	-	-
	0.3502	0.0779	0.9788	0.0207	3.769	10.535
	0.3830	0.1368	0.9563	0.0430	3.183	7.946
	0.4176	0.2135	0.9236	0.0753	2.836	6.273
	0.4341	0.2560	0.9019	0.0964	2.657	5.520
	0.4490	0.2810	0.8768	0.1204	2.333	4.556
	0.4925	0.3211	0.8490	0.1458	2.203	3.798
	0.5554	0.3052	0.8269	0.1656	1.843	2.743

[a]Standard uncertainties u are u(T) = 0.1K, u(x) = 0.001

Table 4. Parameters of Othmer-Tobias correlation for the system water (1) + ethanol (2) + [bmim][Tf_2N] (3).

***T* (K)**	***a***	***b***	R^2
283.15	0.2008	1.3188	0.9986
293.15	0.2370	1.2156	0.9994
303.15	0.2539	1.1408	0.9985
313.15	0.2637	0.9575	0.9976
323.15	0.2777	0.8368	0.9961
333.15	0.2764	0.7968	0.9937

Table 5. UNIQUAC and NRTL binary interaction parameters for water (1) + ethanol (2) + [bmim][Tf_2N] (3) system.

		UNIQUAC parameters		*rmsd (%)*	*NRTL parameters*			*rmsd (%)*
T (K)	*i-j*	*Aij(J.mol^{-1})*	*Aji(J.mol^{-1})*		α	*Aij(J.mol^{-1})*	*Aji(J.mol^{-1})*	
283.2	1-2	10.32	-958.64	0.137	0.3	-1164.25	-2078.99	0.301
	1-3	302.15	4318.68		0.3	16265.83	3851.29	
	2-3	-410.67	760.17		0.3	6055.64	-6293.63	
303.2	1-2	-3910.64	2684.62	0.172	0.3	1404.05	-1619.53	0.228
	1-3	381.75	3947.06		0.3	18957.18	3871.37	
	2-3	-1522.57	364.61		0.3	5284.77	-6366.22	
323.2	1-2	110.41	-1242.19	0.154	0.3	2248.25	-1984.73	0.194
	1-3	876.85	3038.65		0.3	19902.50	2871.24	
	2-3	10692.27	-3402.82		0.3	4866.00	-7076.20	